

# Infrared Spectra of Thermally Degraded Poly(Vinyl Chloride)\*

Robert R. Stromberg, Sidney Straus, and Bernard G. Achhammer

The changes in chemical structure occurring in poly(vinyl chloride) as a result of heating in a vacuum in the range 100° to 400° C were studied using infrared spectrophotometry. The principal changes occurring in the residue during pyrolysis in a vacuum were the formation of unsaturated structures and a change from an aliphatic spectrum to one showing aromatic absorption. The data are used to support a previously proposed mechanism of decomposition for poly(vinyl chloride).

## 1. Introduction

The kinetics of the thermal decomposition of poly(vinyl chloride) in a vacuum have been previously reported [1].<sup>1</sup> Under pyrolytic conditions, poly(vinyl chloride) decomposes predominantly into hydrogen chloride and a colored solid residue. The color of the residue has been attributed to a polyene structure existing after the dehydrochlorination [2]. The role of oxygen in the decomposition mechanism has not yet been resolved although hydroperoxide mechanisms have been proposed [3].

Recently group theory has been applied to the interpretation of the infrared spectra of poly(vinyl chloride) and the spectrum has been analyzed in a comprehensive manner [4]. The head-to-tail arrangement of the monomer units [5], and the alternate arrangements of the chlorine atoms in the plane of the carbon chain [6], with the conclusion that the crystallographic repeating unit consists of two monomer units, were further verified by the work of Krimm and Liang [4]. Polarized spectra were used by Krimm and Liang to make band assignments. Other, more limited analyses of the infrared spectra of poly(vinyl chloride) have also been reported [7, 8]. The branching of poly(vinyl chloride) has been measured [9] by determining the methyl group concentration of the reduced polymer. The application of infrared spectrophotometry to the explanation of the degradation process occurring in poly(vinyl chloride) has, however, not been extensively reported in the literature. Campbell and Rauscher [3] utilized changes in the infrared spectra of poly(vinyl chloride) in a study of the base-accelerated degradation of this polymer. Others [10, 11] limited their studies to changes in only one portion of the spectrum.

This paper describes the results of an investigation in which infrared spectrophotometry was used to study changes in chemical structure occurring in the solid residue during pyrolysis of poly(vinyl chloride) in vacuum.

## 2. Experimental Procedure

Three poly(vinyl chloride) polymers were studied. They were prepared from vinyl chloride monomer as follows:

| Polymer            | Preparation  |
|--------------------|--|
| PVC— $\gamma$ ---- | Initiator— $\gamma$ radiation from 0.3 Curie Co-60 source            |
| PVC—bp----         | Initiator—0.1 mole percent of benzoyl peroxide; 40° C                |
| PVC—azo---         | Initiator—0.02 mole percent of 2,2' azobis (isobutyronitrile); 40° C |

All the polymer samples were powdered by grinding under liquid nitrogen. The white powders were sieved through a 325 mesh screen to a particle size less than 44 microns in diameter.

Specimens of these polymers were pyrolyzed in a vacuum for 30 min at temperatures up to 400° C after outgassing at 110° C for approximately 1 hour. At temperatures above 180° C volatile products were evolved. The color of the residue changed to light brown at the lower pyrolysis temperatures and to dark brown at the more elevated temperatures.

After the exposure to pyrolytic conditions was completed, the degraded powder samples were removed and prepared for infrared analysis. Untreated poly(vinyl chloride) is soluble in only a few solvents, which include cyclohexanone, tetrahydrofuran, dimethyl formamide and to a limited extent, ketones. Some of the degraded material had an even more limited solubility. Cyclohexanone and tetrahydrofuran tend to form hydroperoxides, which decompose easily and may initiate decomposition of the polymer. If these solvents are retained in the polymer film, they also can lead to erroneous conclusions about the structure of the polymer. This is especially true when hydroperoxide breaks down to give carbonyl and hydroxyl groups. Therefore, the solid phase pellet method was used to prepare the material for infrared analysis. Potassium bromide (Harshaw Chemical Co.) was used for the suspending medium

\*Presented at the 8th Annual Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March 1957.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

because it has a refractive index,  $n_D$  of 1.56 which approximates that of untreated poly(vinyl chloride) (1.55). The polymer and the potassium bromide in the ratio of 1 to 50 were mixed in a dry box and the pellets were prepared in the manner described previously [12]. Although the ratio by weight of polymer to potassium bromide was the same for all samples, there was an increase in the molar ratio of degraded polymer to potassium bromide as a result of the loss of hydrogen chloride.

A Perkin-Elmer Model 21 double-beam infrared spectrophotometer with a sodium chloride prism was used for measurements in the 5000 to 670  $\text{cm}^{-1}$  region. For increased resolution a Perkin-Elmer Model 12-B instrument with a lithium fluoride prism was used for measurements in the 3000 to 2600  $\text{cm}^{-1}$  region.

### 3. Infrared Spectra and Discussion

#### 3.1. Untreated Polymers

The infrared spectra of the three poly(vinyl chloride) polymers studied are shown in figure 1. These patterns were obtained by placing a potassium bromide pellet containing the untreated poly(vinyl chloride) in the sample beam and a blank potassium bromide pellet in the reference beam. A commercial polymer, Geon 101<sup>2</sup>, was studied with a lithium fluoride prism in the region of 3000 to 2820  $\text{cm}^{-1}$ . This spectrum is given in figure 2.

The assignments of the principle absorption bands of the basic polymer are given in table 1. Krimm and Liang [4] reported absorptions in the region of 3000  $\text{cm}^{-1}$  that varied slightly from those given in table 1 and figure 2. It is possible that this small difference is a result of the nature and perhaps scatter of the pellet specimen. Krimm and Liang

<sup>2</sup> B. F. Goodrich Chemical Co.

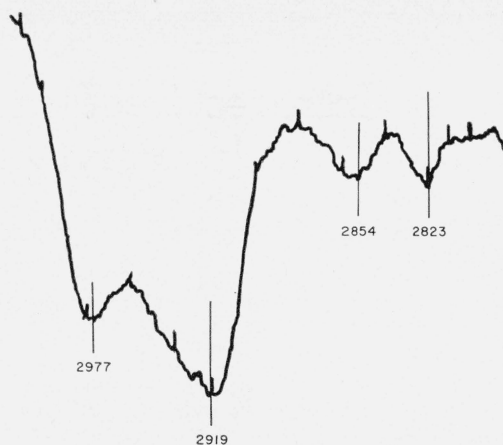


FIGURE 2. Portion of infrared spectrum of Geon-101 PVC using lithium fluoride prism.

TABLE 1. Assignments of absorption bands for untreated poly(vinyl chloride)

| Frequency<br><i>cm</i> <sup>-1</sup> | Assignment   | References |
|--------------------------------------|--|------------|
| 690                                  | C—Cl stretch .....   | 3 4        |
| 833                                  | chain stretch .....  | 4          |
| 963                                  | chain stretch .....  | 4          |
| 1095                                 | perpendicular chain stretch .....                          | 4          |
| 1120                                 | parallel chain stretch .....                               | 4          |
| 1200                                 | CH wag, out of phase .....                                 | 4          |
| 1250                                 | CH bend, in phase .....                                    | 4          |
| 1330                                 | CH bend, out of phase .....                                | 4          |
| 1352                                 | CH <sub>2</sub> wag, in phase .....                        | 4          |
| 1427                                 | CH <sub>2</sub> bend, in phase .....                       | 2,4        |
| 2823                                 | CH stretch, in phase .....                                 | 4          |
| 2854                                 | CH <sub>2</sub> stretch, symmetrical, in phase .....       | 4,13       |
| 2919                                 | CH <sub>2</sub> stretch, asymmetrical, in phase .....      | 4,13       |
| 2977                                 | CH stretch, out of phase, on neighboring CHCl groups ..... | 4          |

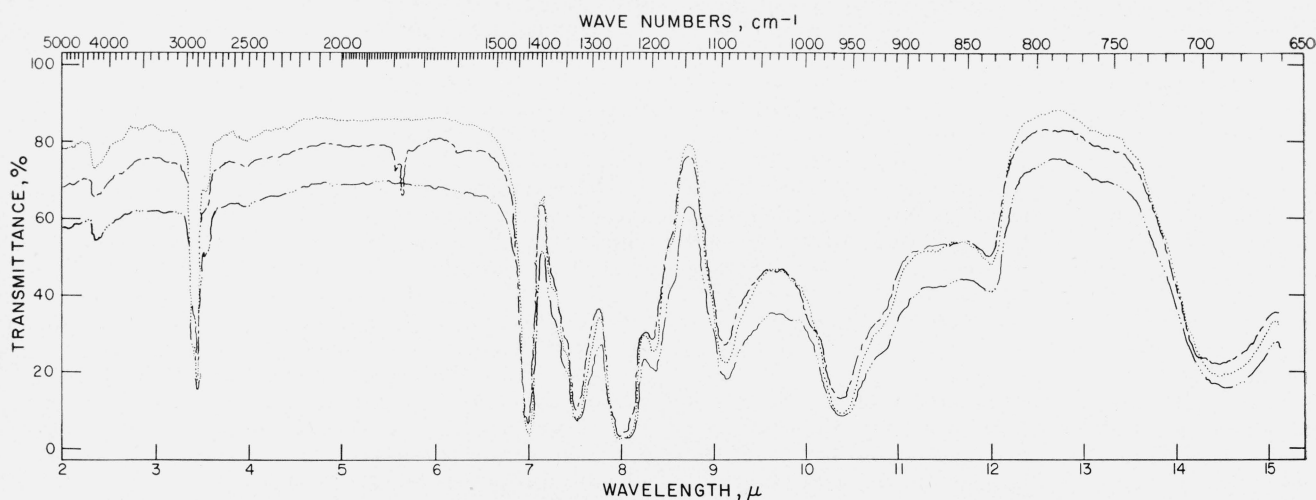


FIGURE 1. Infrared spectra of the poly(vinyl chloride) polymers studied.

..... PVC- $\gamma$   
 ----- PVC-bp  
 - · - · - · - PVC-azo

obtained their spectra from a film and the spectrum shown in figure 2 was obtained from a pellet.

A weak absorption band at  $1590\text{ cm}^{-1}$  is observed in the spectrum of the PVC- $\gamma$  sample. This is assigned to a carbon—carbon double bond stretching vibration [13]. The double bond structure is formed as a result of some dehydrochlorination [1] of the polymer while exposed to the  $\gamma$ -radiation.

The curve obtained from the PVC-bp sample exhibits several absorption bands not observed in the other polymers. The bands at  $1795\text{ cm}^{-1}$  and  $1773\text{ cm}^{-1}$  are assigned to the carbonyl vibration of the catalyst, benzoyl peroxide [13]. The band at  $1733\text{ cm}^{-1}$  is probably from the carbonyl stretching vibration of an aldehyde or ketone [13], formed from interaction of the catalyst with vinyl chloride. Benzoyl peroxide shows an absorption [13] near  $1000\text{ cm}^{-1}$  and the band at  $990\text{ cm}^{-1}$  is probably from unreacted catalyst.

### 3.2. Spectra of Poly(Vinyl Chloride) After Pyrolysis

Figure 3 shows the spectra of PVC-bp residue after pyrolysis for 30 min in a vacuum at several temperatures. The spectra are progressively altered as a result of increasing the pyrolysis temperature. There is considerable radiation scatter for the pellets of the samples pyrolyzed at higher temperatures where the refractive index of the more highly degraded colored specimens did not match that of the potassium bromide. The samples were pretreated by heating at  $110^\circ\text{C}$  in a vacuum for approximately 1 hour. The only changes observed in the spectrum of the material after this treatment was the disappearance of the peroxide bands at  $1795$  and  $1773\text{ cm}^{-1}$ , indicating removal of the unreacted catalyst by this pretreatment. At temperatures up through  $250^\circ\text{C}$ , the infrared pattern, although somewhat altered, is easily identified as that of poly(vinyl chloride). At temperatures of

the order of  $300^\circ\text{C}$  and higher, there is a marked over-all departure from the spectrum of poly(vinyl chloride). It was shown in a previous study [1] that at approximately  $300^\circ\text{C}$  practically all of the chloride atoms have been removed from the polymer as HCl without any apparent appreciable breakdown of the polymer chain. This removal of the highly electronegative halogen from the chain could cause frequency shifts in some absorption bands as well as other spectral changes resulting from the new structural configurations. Substantial breakdown of the polymer chain occurs at  $400^\circ\text{C}$  [1].

In the region of the carbon—hydrogen stretching absorption,  $3000\text{ cm}^{-1}$ , a new band is formed at  $3030\text{ cm}^{-1}$  that may be associated with the carbon—hydrogen stretching vibration from an unsaturated carbon—carbon linkage [13]. The intensity of this band increases with increasing temperatures of pyrolysis. Nonconjugated carbon—carbon double bonds are suggested by the absorption at  $1670\text{ cm}^{-1}$  [13]. The absorption band at  $1610\text{ cm}^{-1}$  is assigned to the carbon—carbon double bond stretching vibration for conjugated bonds, either aromatic or aliphatic or both [13].

The shoulder at  $1590\text{ cm}^{-1}$  is assigned to the carbon—carbon double bond vibration of an aromatic ring [13]. A resonance splitting of the absorption bands with the appearance of one band near  $1600\text{ cm}^{-1}$  and one near  $1500\text{ cm}^{-1}$  occurs when there are three unsaturated carbon—carbon vibrations in a ring [13]. The bands at  $1610$  and  $1500\text{ cm}^{-1}$  are therefore assigned, at least in part, to an aromatic structure. The broad absorption bands at  $880$ ,  $820$ ,  $750$ , and  $700\text{ cm}^{-1}$  are present in the spectra of asphalts, heavy petroleum oil fractions, coal, etc., [14] and indicate the presence of aromatic structures, with the latter two indicating carbon—hydrogen out-of-plane deformations of monosubstituted aromatic groups [13]. The absence of aromatic structural bands in the untreated poly(vinyl chloride) and

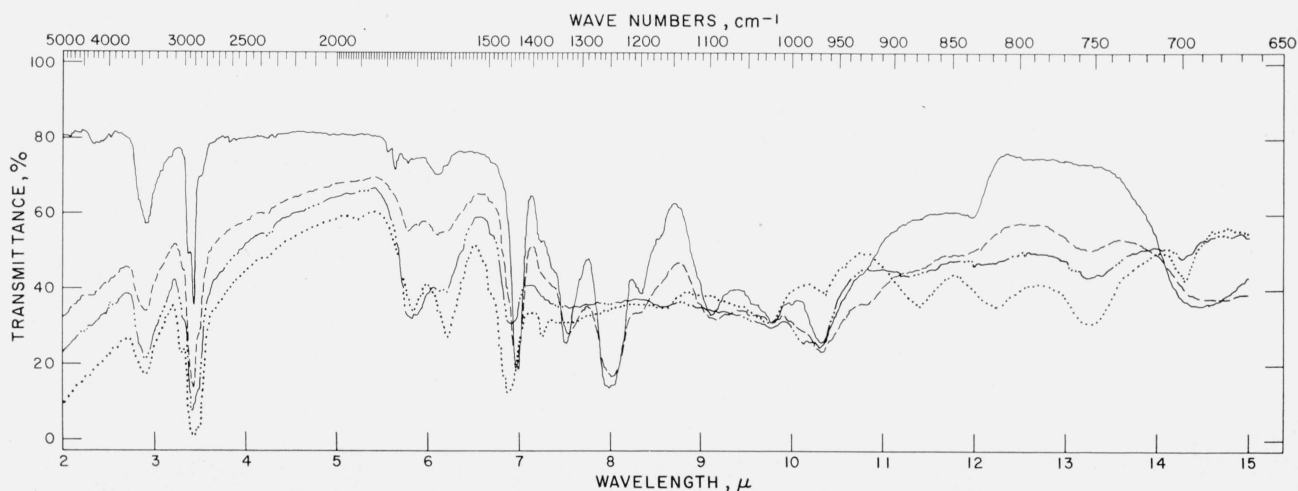


FIGURE 3. Infrared spectra of PVC-bp after 30 minutes' pyrolysis.

— Untreated  
 — — —  $255^\circ\text{C}$   
 - - - - -  $300^\circ\text{C}$   
 .....  $400^\circ\text{C}$

their appearance and increase in intensity as a result of higher degradative temperatures can be readily observed.

The absorption at  $1720\text{ cm}^{-1}$  indicates the presence of carbonyl vibrations. This band did not appear to any appreciable extent when the pyrolyzed material was stored under an inert atmosphere. As this spectral change does not occur at room temperature in untreated polymer, it appears that the double bonds in the degraded polymer are subject to attack by atmospheric oxygen, forming such oxygenated structures.

The shifting of the carbon—hydrogen vibration of  $\text{CH}_2$  [3] from  $1430\text{ cm}^{-1}$  in the spectrum of untreated polymer to  $1455\text{ cm}^{-1}$  for the more highly decomposed samples may be a result of a loss of the chlorine atoms or an increase in the  $\text{CH}_3$  concentration [13]. The band at  $1380\text{ cm}^{-1}$  in the most highly degraded material may be assigned to the carbon—hydrogen deformation frequency for the aliphatic  $\text{C—CH}_3$  bond [13].

The removal of the band at  $690\text{ cm}^{-1}$ , assigned to the  $\text{C—Cl}$  stretching vibration [3, 4], from the spectrum of the sample pyrolyzed at  $300^\circ\text{C}$  correlates with mass spectrometer and weight loss measurements [1] which showed that almost all the chlorine atoms were removed from the polymer at this temperature.

The infrared spectra of the PVC- $\gamma$  polymer after pyrolysis at several temperatures are shown in figure 4. The changes in the spectra as a result of increasing the pyrolysis temperature are similar to those observed for the PVC-bp material. The spectrum of the specimen degraded at  $250^\circ\text{C}$  can be readily identified as poly(vinyl chloride). Increasing the temperature to  $275^\circ\text{C}$  gives a spectrum, from  $1400$  to  $650\text{ cm}^{-1}$  that is different from the spectrum of poly(vinyl chloride). This is probably caused by the almost complete removal of chlorine atoms as shown by the absence of a band at  $690\text{ cm}^{-1}$ . The

presence of the conjugated aromatic structure is revealed in the spectra of the specimens pyrolyzed at  $342^\circ$  and  $400^\circ\text{C}$  by the bands at  $880$ ,  $820$ ,  $750$ ,  $700\text{ cm}^{-1}$  and the shoulder at  $1490\text{ cm}^{-1}$ . There is also absorption caused by aromatic structure in the spectrum of the specimen pyrolyzed at  $275^\circ\text{C}$ .

The spectra of the pyrolyzed PVC—azo sample is shown in figure 5. The same general observations made with the PVC—bp and PVC— $\gamma$  polymers also apply to this material. However, this sample is observed to have undergone more degradation at a given temperature than the other two polymers did. For example, no  $\text{C—Cl}$  stretching band at  $690\text{ cm}^{-1}$  remains in the specimen pyrolyzed at  $253^\circ\text{C}$ , while this band is relatively intense for the PVC—bp polymer, pyrolyzed at the same temperature. This is in agreement with the faster rate of decomposition, as measured by rate of weight loss for this material as previously reported [1]. This faster rate was attributed to unreacted catalyst remaining in the sample.

The pyrolysis of poly(vinyl chloride) produces volatile products and a solid residue. At  $400^\circ\text{C}$  some of these products are volatile at the temperature of pyrolysis but not at room temperature. This portion is a brown, waxlike material at room temperature. The spectrum of this wax is similar to that of the more highly degraded specimens observed earlier and probably consists of fragments of the dehydrochlorinated polymer. The  $\text{C—Cl}$  band at  $690\text{ cm}^{-1}$  is absent, accounting for a flat spectrum observed at the lower wave numbers. A broad carbonyl band at  $1730\text{ cm}^{-1}$  is probably the result of the oxidation of double bond structures following the pyrolysis. The  $\text{CH}$  vibration [3] in  $\text{CH}_2$  is shifted from  $1430\text{ cm}^{-1}$  in the original material to  $1470\text{ cm}^{-1}$ . A band at  $1380\text{ cm}^{-1}$ , assigned to the  $\text{C—H}$  deformation for the aliphatic  $\text{C—CH}_3$  bond [13], is present in this spectrum as well as in the spectrum of the residue of the material pyrolyzed at  $400^\circ\text{C}$ . Although there are weak bands at  $700$ ,

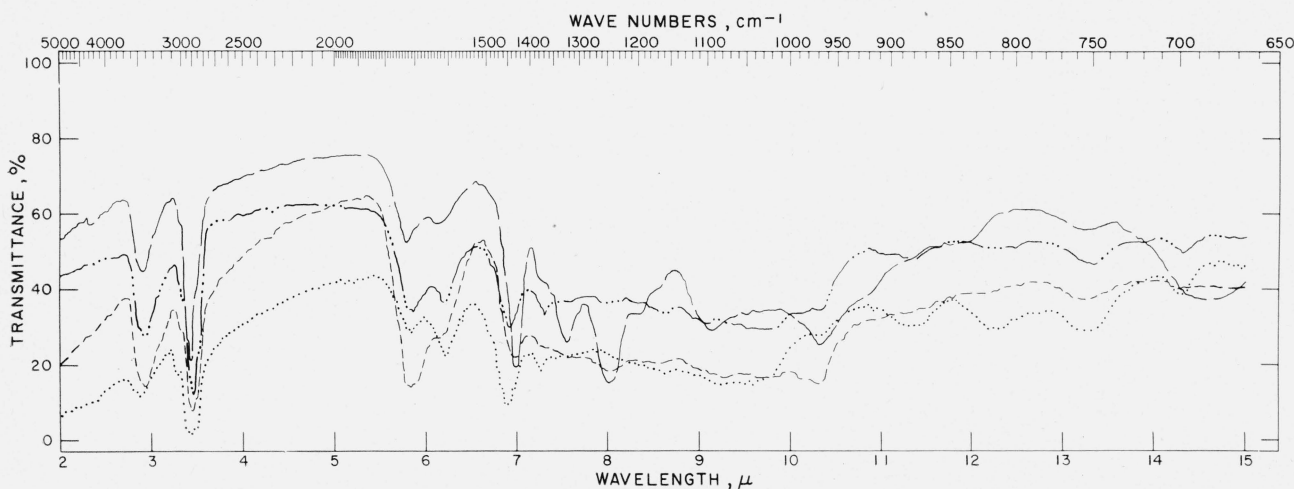


FIGURE 4. Infrared spectra of PVC- $\gamma$  after 30 minutes' pyrolysis.

—  $250^\circ\text{C}$   
 - - -  $275^\circ\text{C}$   
 - · - · -  $340^\circ\text{C}$   
 · · · · ·  $400^\circ\text{C}$



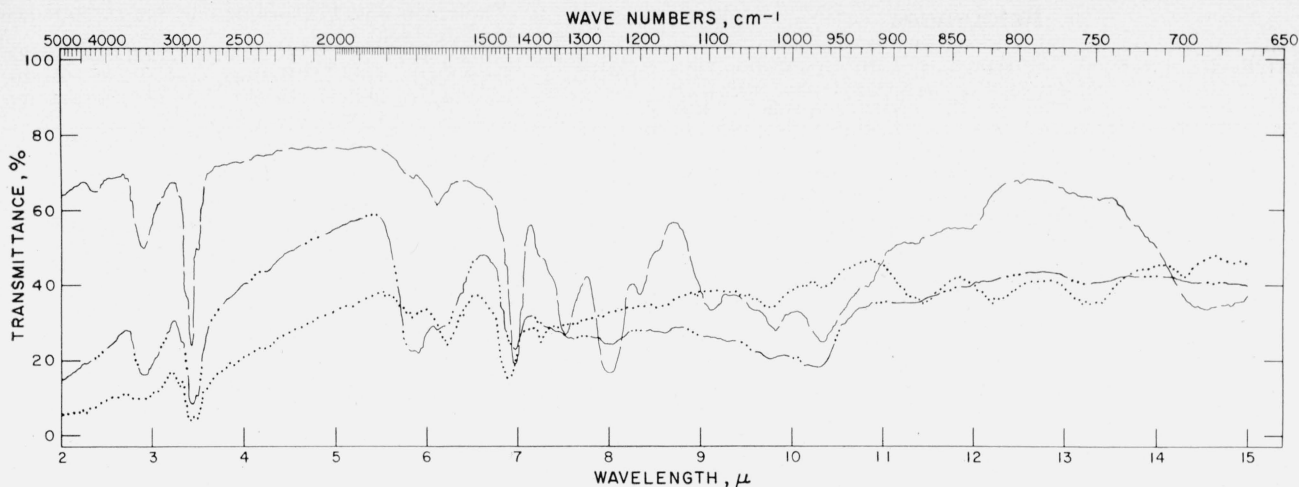


FIGURE 5. Infrared spectra of PVC-azo after 30 minutes' pyrolysis.

— 220° C  
 - - - 255° C  
 ..... 400° C

720, and 755  $\text{cm}^{-1}$ , the relatively intense bands assigned to aromatic structures in the spectrum of the residue of the material pyrolyzed at 400° C are absent from this spectrum. The differences between the spectrum of the residue and the spectrum of the waxlike material are attributed to the different molecular weights of these portions.

#### 4. Conclusions

Specimens pyrolyzed in a vacuum at temperatures up to 400° C yielded some spectra that were decidedly different from the original material and which varied from each other depending upon the temperature. The volatile products obtained from the poly(vinyl chloride) polymers at temperatures up to 300° C consisted primarily of HCl and a few mole percent of benzene [1]. At 400° C, the volatile products produced from the dehydrochlorinated polymer consisted, in addition, of larger quantities of benzene and various hydrocarbons. The principal alterations in the infrared spectra of these degraded specimens were loss of chlorine atoms, with complete removal at temperatures near 300° C, establishment of double bond character, both aliphatic and aromatic, and a possible increase in  $\text{CH}_3$  concentration. A variety of carbonyl structures is formed when the degraded material is allowed to stand exposed to the air for several days at room temperature. Within the limits of this technique the spectral changes are independent of polymerization initiators used.

The mechanism of the decomposition appears to be a removal of chlorine as HCl in such a manner as to form a conjugated polyene structure, even when only small quantities of chlorine have been removed. No infrared evidence was found for hydroperoxides. It appears reasonable, therefore, that oxygen does not play a direct role in the dehydrochlorination process of the systems studied here, but adds to the double bond structure, producing

the oxygenated structures observed. This action may further degrade the polymer by reducing the size of the chain. The infrared technique was, however, insensitive to measurement of chain length, although the apparent rise in methyl group concentration is an indication of an increased number of chain ends.

The formation of aromatic structures in the spectra of the degraded aliphatic poly(vinyl chloride) correlates with the presence of benzene in the volatile products of such decomposition reactions [1]. This indicates that an aliphatic conjugated structure is present at chain ends. This structure can occur as a result of dehydrochlorination at the original ends, either by initiation or termination, or by scission of an internal portion of a dehydrochlorinated chain. The dehydrochlorination reaction that has been previously proposed [1] would allow a free radical at the end of a polyene group in either instance. As a result of kinetic motion, various cyclic configurations are formed. Because of resonance considerations, benzene is the most stable structure, and as a result of this stabilization, the carbon-carbon bond alpha to the benzene ring is weakened and breaks, evolving benzene as a product. The more complete removal of chlorine at the higher temperatures, together with the increased opportunity for chain cleavage at these elevated temperatures, yields a more aromatic structure. Moreover, the material that is volatile at the temperature of pyrolysis but not at room temperature apparently consists of short aliphatic segments of the residue.

The authors express appreciation to the following members of the National Bureau of Standards: James E. Stewart for his suggestions regarding some of the interpretations and for obtaining some of the spectra, and Mary R. Harvey and Mary K. Wharton for preparing some of the spectra.

## 5. References

- [1] R. R. Stromberg, S. Straus, and B. G. Achhammer, Thermal decomposition of poly(vinyl chloride) in a vacuum (presented at the 139th meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956).
- [2] C. S. Marvel, Synthetic polymers of organic chemistry, an advanced treatise, vol. I, p. 754, edited by Gilman (John Wiley & Sons, Inc., New York, N. Y., 1943).
- [3] J. E. Campbell and W. H. Rauscher, *J. Polymer Sci.* **18**, 461 (1955).
- [4] S. Krimm and C. Y. Liang, *J. Polymer Sci.* **22**, 95 (1956).
- [5] C. S. Marvel, J. H. Sample, and M. F. Ray, *J. Am. Chem. Soc.* **61**, 324 (1939).
- [6] C. S. Fulla, *Chem. Revs.* **26**, 143 (1940).
- [7] H. W. Thompson and P. Torkington, *Proc. Roy. Soc. (London)* [A] **184**, 21 (1945).
- [8] H. W. Thompson and P. Torkington, *Trans. Faraday Soc.* **41**, 246 (1945).
- [9] J. D. Cotman, Jr., *Ann. N. Y. Acad. Sci.* **57**, 417 (1953).
- [10] A. L. Scarbrough, W. L. Kellner, and P. W. Rizzo, *Modern Plastics* **29**, 111 (1952); Polymer degradation mechanisms, p. 95, NBS Circ. 525 (1953).
- [11] V. W. Fox, J. G. Hendricks, and H. J. Ratti, *Ind. Eng. Chem.* **41**, 1774 (1949).
- [12] M. R. Harvey, J. E. Stewart, and B. G. Achhammer, *J. Research NBS* **56**, 225 (1955) RP2670.
- [13] L. J. Bellamy, *The infrared spectra of complex molecules* (John Wiley & Sons, Inc., New York, N. Y., 1954).
- [14] J. Linnig and J. E. Stewart, *J. Research NBS* **59**, 27 (1957) RP2771.

WASHINGTON, July 24, 1957.